

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO WATER-BASED PROTECTIVE COATING COMPOSITIONS

(71) We, HERCULES INCORPORATED, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 910 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to water-based protective coating compositions and more particularly to such compositions comprising a particular hydroxyethyl cellulose (HEC) which imparts substantially increased biostability to the compositions. One embodiment of this invention relates to paints and more specifically latex or emulsion paints.

Although HEC has enjoyed a large use for many years in protective coatings as a suspending agent and thickener it would be substantially improved for this use if its susceptibility to biodegradation could be reduced.

Biodegradation of HEC is due to hydrolytic cleavage of the linkages between anhydroglucose units, catalyzed especially by the enzyme cellulase (i.e. β - 1,4 - glucan 4-glucanohydrolase). This enzyme is associated with a large variety of spores and bacteria which are present in the air and in water. If an aqueous solution, thickened with HEC, becomes contaminated with one of these microorganisms, the cellulase present catalyzes the hydrolysis of the HEC, lowering the viscosity

of the solution. The rate at which the viscosity is lowered depends, among other things, on the enzyme concentration and as is disclosed in greater detail hereinafter is due to the number and distribution of unsubstituted anhydroglucose units in the cellulose polymer. This enzyme concentration increases rapidly as the microorganism multiplies. On storage, the viscosities of such contaminated solutions usually are substantially reduced, and in protective coating compositions (e.g. paints) such viscosities sometimes become so low that the compositions are no longer useful. Biostability is the resistance to this degradation and to the resultant viscosity reduction. Thus by biostable is meant that the HEC retains a substantial amount of its initial viscosity over long periods of exposure to air- or water-borne biological agents whose presence can substantially reduce the molecular weight of the HEC. A low percent anhydroglucose units unsubstituted in the HEC molecule as contrasted with prior art HEC is a measure of this biostability.

According to one aspect of the invention there is provided a protective coating composition comprising a film former dispersed in water and a suspending agent consisting of a hydroxyethyl cellulose which has an M.S. (as hereinafter defined) in the range of 1.5 to 10 and a maximum percentage unsubstituted anhydroglucose unit content as defined by the following tabulation in which each M.S. range includes the first value but excludes the last value:

Maximum
% Anhydroglucose
Units Unsubstituted

M.S. Range

	11	1.5 and all values between 1.5 and 2.0
75	9	2.0 and all values between 2.0 and 2.5
	7	2.5 and all values between 2.5 and 3.0
	5.5	3.0 and all values between 3 and 3.5
	4	3.5 and all values between 3.5 and 4.0
	2	4.0 and all values between 4.0 and 5.0
80	1	5.0 and all values between 5.0 and 10

[Price 25p]

According to a further aspect of the invention there is provided a method of increasing the biostability of a water-based protective coating composition, said composition comprising a film former dispersed in water and a suspending agent consisting of a hydroxyethyl cellulose, comprising using as the sus-

pending agent a hydroxyethyl cellulose having an M.S. (as hereinafter defined) in the range 1.5 to 10 and a maximum percentage unsubstituted anhydroglucose unit content as defined by the following tabulation in which each M.S. range includes the first value but excludes the last value:

15	M.S. Range	Maximum % Anhydroglucose Units Unsubstituted
20	1.5 and all values between 1.5 and 2.0 2.0 and all values between 2.0 and 2.5 2.5 and all values between 2.5 and 3.0 3.0 and all values between 3 and 3.5 3.5 and all values between 3.5 and 4.0 4.0 and all values between 4.0 and 5.0 5.0 and all values between 5.0 and 10	11 9 7 5.5 4 2 1

25 "M.S." (molecular substitution) as used herein with reference to the HEC means the average number of molecules of ethylene oxide combined per anhydro-glucose unit of the cellulose. This was determined by the Morgan modification of the Zeisel method—P. W. Morgan, Ind. Eng. Chem. 18, 500 (1946).

The following examples illustrate specific embodiments of this invention. These examples are not intended to limit the present invention beyond the scope of the appended claims. Percent, parts and ratios are by weight unless otherwise indicated. In these examples water soluble HEC was used as a thickener in various protective coating compositions (latex paints) and susceptibility of the HEC to enzymatic degradation in the compositions was determined by the usual method, namely by measuring the decrease in viscosity of the protective coating compositions after various time intervals. Desirably a latex paint at the time of use will have a viscosity of at least about 70 Krebs units (Ku). In Examples 1—4 the enzyme used was that which is commercially available under the tradename "Cellase 1000" (Wellerstein Co.) the chief ingredient of which is cellulase or β -1,4-glucan 4-glucanohydrolase. In Examples 5 and 6 the samples of paints were inoculated with a live culture of *Aspergillus niger* which forms enzymes as it grows. In each example the samples were stored in closed containers at 25° C. and their viscosities measured periodically. The components of these formulations are commercially available or can be readily made by conventional techniques from available chemicals.

EXAMPLES 1 & 2.

Vinyl Acetate-Dibutyl Maleate Latex Paint
Examples 1 and 2 contrast the viscosity retention of vinyl acetate-dibutyl maleate copolymer latex paint formulations given below

using as thickener HEC of this invention (Example 1) and prior art HEC (Example 2) and using 0.5 ppm. of the enzyme Cellase 1000 in each example. Except for the type of HEC used the formulations and preparation were identical.

	Components	Concentration in Parts by Weight	
	Flexbond	735.0	75
	PMA—18	0.9	
	(a) HEC (2% conc.)	597.4	
	Tanol 731 (25% conc.)	13.0	
	Igepal CO—710	11.7	
	Ethylene glycol	73.5	80
	Colloid 60	7.0	
	Texanol (Registered Trade Mark)	29.4	
	TiPure R—900	735.0	
	Nyrul 300 (Registered Trade Mark)	73.5	85
	Atomite	441.7	
	Celite 281 (Registered Trade Mark)	102.7	
	Water	763.5	90

(a) The formulations in Examples 1 and 2 were identical except for the type of HEC used. In Example 1 the HEC used was the type of this invention, specifically % anhydroglucose units unsubstituted of 6.9 and M.S. 2.5. In Example 2 the HEC used was the type of the prior art, specifically % anhydroglucose units unsubstituted of 11.8 and M.S. 2.5.

All of the above components in Examples 1 and 2 except the first three were ground together in a Cowles dissolver at 4400 rpm for 10 minutes. Then the agitation speed was reduced to about 2000 rpm or slower and the first three components were slowly worked in.

Flexbond 800 is a commercial vinyl acetate-

dibutyl maleate copolymer latex. PMA—18 is phenyl mercuric acetate. Tamol 731 is the sodium salt of a polymeric carboxylic acid, an anionic dispersant. Igepal CO—710 is nonylphenoxy poly(ethyleneoxy)ethanol, a surfactant. Colloid 60 is a hydrocarbon containing silica, a defoamer. Texanol is a water immiscible 12-

carbon ester alcohol, a coalescing agent. TiPure R—900 is TiO_2 , a pigment. Nyral 300 is talc extender, a pigment. Atomilic is CaCO_3 . Celite 281 is diatomaceous earth.

Viscosity data and further details appear in Table I below.

TABLE I(a)

			TABLE 4(a)						
			Viscosity (d)						
			After (days)						Decrease in KU after 30 days
Ex.	Type HEC	M.S.	Zero	1	8	13	20	30	
1	This invention (b)	2.5	90	90	90	90	89	89	1.0
2	Prior art (c)	2.5	86	84	82	81	78	76	10.0

(a) 0.5 ppm. (based on the paint formulation) of the enzyme Cellase 1000 and a pH of 8 were used in each example.

(b) % anhydroglucose units unsubstituted 6.9; M.S. 2.5

(c) % anhydroglucose units unsubstituted 11.8; M.S. 2.5

(d) Viscosities were determined on a Krebs-Stormer viscometer at 25°C. and are expressed in Krebs units (KU).

15 EXAMPLES 3 & 4.

Acrylic Polymer Latex Paints

Examples 3 and 4 contrast the viscosity retention of acrylic polymer latex paint formulations given below using as thickener HEC

of this invention (Example 3) and prior art HEC (Example 4) and using 1.0 ppm. of the enzyme Cellase 1000 in each example. Except for type HEC used the formulations and preparation were identical.

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Components		Concentration in Parts by Weight
Group 1		
Tamol 731 (25%)		37.5
Topco NDW		7.5
Propylene Glycol		228.0
TiPure R—900		936.0
Water		291.0

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Group 2

Propylene Glycol	381.0
Rhoplex AC 490	1791.0
Nopco NDW	7.5
Super Ad-It	3.3
Butyl Cellosolve	84.9
Triton GR—7	7.5
(a) HEC, 2.0% aqueous solution	161.5
(Nopco, Cellosolve and Triton are all Registered Trade Marks).	

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(a) The formulations in Examples 3 and 4 were identical except for the type of HEC used. In Example 3 the HEC used was the type of this invention, specifically % anhydroglucose units unsubstituted of 6.9 and M.S. 2.5. In Example 4 the HEC used was the type of the prior art, specifically % anhydroglucose units unsubstituted of 11.8 and M.S. 2.5.

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- The first group of components in Examples 3 and 4 above were ground together in a Cowles dissolver at 4000 rpm. for 20 minutes. Then the agitation speed was reduced to about 2000 rpm. or slower and the components in the second group were slowly worked in.
- Rhoplex AC 490 is a commercial acrylic latex. Nopco NDW is a defoamer. Super Ad-It is di(phenylmercuric) dodecyl succinate, a preservative. TiPure R—900 is TiO_2 , a pigment. Triton GR—7 is dioctyl sodium sulfosuccinate, a surfactant. Tamol 731 is the sodium salt of a polymeric carboxylic acid, an anionic dispersant.
- Viscosity data and further details appear in Table II below.

TABLE II(a)

Ex.	Type HEC	M.S.	Viscosity (d)					Decrease in KU after 28 days
			After (days)					
			Zero	5	13	18	28	
3	This invention (b)	2.5	76	74	72	72	72	4
4	Prior Art (c)	2.5	76	69	65	63	61	15

- (a) 1.0 ppm. (based on the paint formulation) of enzyme Cellase 1000 and a pH of 8.2 were used in each example.
- (b) % anhydroglucose units unsubstituted 6.9; M.S. 2.5
- (c) % anhydroglucose units unsubstituted 11.8; M.S. 2.5
- (d) Viscosities were determined on a Krebs-Stormer viscometer at 25°C. and are expressed in Krebs units (KU).

EXAMPLES 5 & 6.

- Ethylene-Vinyl Acetate Latex Paint
- Examples 5 and 6 contrast the viscosity retention of ethylene-vinyl acetate copolymer latex paint formulations given below using as

thickener HEC of this invention (Example 5) and prior art HEC (Example 6) and using a living culture of *Aspergillus niger* in each example.

	Components	Concentration in Parts by Weight
30	Tamol 850	35.0
	Igepal CO—610	20.0
	Ethylene glycol	125.0
	Colloid 677	20.0
	Texanol	50.0
35	TiPure R—911	1250.0
	Zcolex 80 (Registered Trade Mark)	125.0
	Carbium	750.0
	Celite 281	175.0
	Water	1000.0
40	Aircoflex 510	1250.0
	(a) HEC, 3% aqueous solution	772.0

- (a) The formulations in Ex. 5 & 6 were identical, except for the type of HEC used. In Ex. 5 the HEC used was the type of this invention, specifically % anhydroglucose units unsubstituted of 6.9 and M.S. 2.5. In Ex. 6 the HEC used was the type of the prior art, specifically % anhydroglucose units unsubstituted of 11.8 and M.S. 2.5.

- 5 All of the components in Examples 5 and 6 above except the last three were ground together in a Cowles dissolver at 4000 rpm. for 20 minutes. Then the agitation speed was reduced to about 2000 rpm. or slower and the last three components were slowly worked in.
- 10 Tamol 850 is the sodium salt of a polymeric carboxylic acid, an anionic dispersant. Igepal CO-710 is nonyl phenoxy poly(ethyleneoxy) ethanol, a surfactant. Colloid 677 is a defoamer. Texanol is 3 - hydroxy - 2,2,4-trimethylpentyl isobutyrate. TiPure R-911 is TiO₂, a pigment. Zeolex 80 is a hydrated sodium silico aluminate, a pigment extender. Carbiun is calcium carbonate, a flattening agent. Celite 281 is diatomaceous earth. Aircoflex 510 is an ethylene-vinyl acetate copolymer latex.
- 20 900 g. portions of these paints were inoculated with the same quantity (2 cc.) of the same living culture of *Aspergillus niger*, stored in closed containers at 25°C. and the viscosity was measured periodically.
- 25 Viscosity data and further details appear in Table III below.

TABLE III(a)

Ex.	Type HEC	M.S.	Viscosity (d)							Decrease in KU after 95 days
			After (days)							
			Zero	4	26	34	42	60	95	
5	This invention (b)	2.5	90	90	90	86	87	86	85	5
6	Prior Art (c)	2.5	90	88	86	84	83	82	79	11

(a) 2 cc. of the living culture of *Aspergillus niger* and a pH of 7.9 were used in each example

(b) % anhydroglucose units unsubstituted 6.3; M.S. 2.5

(c) % anhydroglucose units unsubstituted 10.3; M.S. 2.5

(d) Viscosities were determined on a Krebs-Stormer viscometer at 25°C. and are expressed in Krebs units (KU).

These tests represent actual conditions where the organism lives in the paint and forms enzyme as it grows.

30 It is readily apparent from the foregoing Examples that in two different type paint formulations there was substantially no loss in viscosity after approximately one month when using the HEC of this invention as a thickener, whereas when prior art HEC was used in the same paint formulations there was a loss in viscosity of about 10-15 Ku.

35 The type hydroxyethyl cellulose useful in the present invention is critical. In order to characterize the HEC of this invention, it will be helpful to discuss structural factors which influence the enzymatic degradation of water soluble cellulose derivatives. Cellulose consists of straight chains of β -anhydroglucose units held together by glucosidic linkages. In water soluble cellulose derivatives, it is believed that cleavage due to enzymatic

hydrolysis occurs at linkages between two anhydroglucose units at least one of which is unsubstituted—R. G. H. Siu in Ott and Spurlin, *Cellulose and Cellulose Derivatives*, p. 183, Interscience, N.Y. 1954. Others believe that chain scission occurs more rapidly at linkages between two unsubstituted glucose units—M. G. Wirick, *J. Polymer Science A-1* 6, 1705 (1968). The intrinsic fluidity change, $\Delta [\eta]$, which has been shown to be a measure of the number of chain breaks (L. F. McBurney in Ott and Spurlin, *Cellulose and Cellulose Derivatives*, pp. 109-111, Interscience, N.Y. 1954), is directly proportional to the content of unsubstituted anhydroglucose units if the weight of enzyme per anhydroglucose unit of the HEC is kept constant. Table IV hereinafter illustrates this for conventionally prepared water soluble HEC of different M.S. values.

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TABLE IV
Conventional HEC

Example	7	8	9	10	11
M.S.	1.47	1.82	2.44	2.96	5.13
% Unsubstituted glucose (a)	22.8	13.15	11.9	7.3	5.8
$\Delta[\phi]$ after 24 hrs. at 25°C. (b)	1.34	0.85	0.69	0.47	0.23

(a) unsubstituted glucose units per 100 glucose units

(b) intrinsic fluidity change after 24 hours at 25°C. for 0.0055 g. mole/l. of HEC and 0.008 g./l. of enzyme (Cellase 1000).

5 The content of unsubstituted glucose units is determined by first hydrolyzing the cellulose derivative in aqueous H_2SO_4 —ASTM Method D1915—63, Vol. 15, p. 651. The unsubstituted glucose in the hydrolyzate is determined by enzymatically oxidizing the unsubstituted glucose to gluconic acid and H_2O_2 . In the presence of horseradish peroxidase, the H_2O_2 oxidizes o-dianisidine to a colored form. The amount of color developed is a measure of the unsubstituted glucose—R. R. Barton, *Analytical Biochemistry* 19, 258—60 (1966). Since the intrinsic fluidity change (a good

measure of the number of chain breaks) is approximately proportional to the content of unsubstituted glucose, it is apparent that the susceptibility of the cellulose derivative for enzymatic degradation is determined by the amount of unsubstituted glucose units present.

The type HEC applicable in this invention is defined and contrasted with prior art HEC in Table V and the accompanying figure (graph) with reference to the approximate percent anhydroglucose units unsubstituted for the M.S. values given.

TABLE V

M.S. Range ⁽¹⁾	% Anhydroglucose Units Unsubstituted	
	This Invention	Prior Art
	Maximum	Minimum
1.5 and all values between 1.5 and 2.0	11	12.5
2.0 " " " " 2.0 and 2.5	9	10
2.5 " " " " 2.5 and 3.0	7	8
3.0 " " " " 3 and 3.5	5.5	6.5
3.5 " " " " 3.5 and 4.0	4	5
4.0 " " " " 4.0 and 5.0	2	3
5.0 " " " " 5.0 and 10	1	2

⁽¹⁾ Each range includes the first value but excludes the last value (e.g. 1.5 and all values up to but not including 2 are meant for the first range).

The particular HEC which can be used in accordance with this invention has been prepared heretofore, so the HEC and preparation thereof are known and are not per se a part of this invention. For the sake of ease of understanding and completeness, preferred methods of preparing the HEC will be described herein. HEC processes set forth in U.S. Patent Nos. 3,131,176 and 3,131,177 are two of such methods. A critical condition for preparing suitable HEC is that the major part of the hydroxyethylation be carried out using a low alkali/cellulose ratio. However, because of the crystalline nature of cellulose it is necessary to use an alkali/cellulose ratio of at least 0.2/1 and preferably 0.3/1—0.4/1 to decrease the crystallinity and prepare an HEC of the desired good water solubility on reaction with ethylene oxide and this is known in the art. Both of these conditions are met by hydroxyethylating in two stages using a conventional alkali/cellulose ratio in the first stage and a substantially lower alkali/cellulose ratio in the second stage. The alkali/cellulose ratio in the first stage is at least 0.2/1 and can be 0.8/1 or even higher as the artisan knows, but preferably is 0.3/1—0.4/1 particularly for this invention. In the second stage the alkali/cellulose ratio is not in excess of 0.1/1, preferably 0.03/1—0.08/1, but ratios as low as 0.01/1 and even 0.005/1 can be used. The first stage may be defined as hydroxyethylating to an M.S. not in excess of 1.0 and preferably not in excess of 0.8, the second stage being the remainder of the hydroxyethylation to the final M.S. desired which is 1.5—10 but more often 1.5—3. Amounts of alkali specified herein are based on NaOH.

The various other process conditions for preparing HEC useful in this invention are not critical and are well known in this art, so that the artisan having the foregoing disclosure relative to criticality of alkali/cellulose ratio range values will have no difficulty in obtaining suitable HEC for practicing this invention. Also unimportant and well known are the other process conditions including e.g. whether or not the HEC is purified between the first and second stages by removing substantially all of the alkali and other impurities therefrom, type alkali, diluent (if any), water/cellulose ratio, type cellulosic material and so

forth. A preferred process of preparing HEC useful in this invention comprises reacting ethylene oxide with cotton linters to an hydroxyethyl M.S. not exceeding 0.8 in the presence of sodium hydroxide (within the alkali/cellulose ratio ranges disclosed herein-before), tertiary butanol, water, neutralizing the desired amount of the sodium hydroxide, continuing the hydroxyethylation to the M.S. desired without purifying the HEC intermediate product, and then purifying the HEC final product (purification being preferred but not necessary). Without in any way limiting this invention the details of a typical process of preparing HEC useful in this invention according to one embodiment thereof comprises the following:

A reaction mixture of

1.0 part cellulose	
0.8 part isopropanol	
9.4 parts tertiary butyl alcohol	
0.3 part acetone	75
1.6 parts water	
0.325 part NaOH and	
0.43 part ethylene oxide	

was stirred in a pressure vessel from which air had been displaced by nitrogen. The temperature was raised to 70° C. in 0.5 hour and kept at 70° C. for 2.5 hours. Then the temperature was lowered to 50° C. and sufficient HNO₃ was added to lower the NaOH/cellulose from 0.315 to 0.06. At this point the M.S. was approximately 1.0. 0.86 Part of ethylene oxide was added and the reaction was completed in three more hours at 70° C. The product was purified by neutralizing the remaining alkali and washing free of salts and by-product glycols with 80% acetone. It had excellent water solubility and an M.S. of 2.9. Another HEC product of M.S. 2.9 was prepared by prior art process, that is all of the ethylene oxide was added at the outset. Enzymatic degradation tests were made on each of the HEC products in 1% aqueous solution buffered to pH 5.5. The enzyme (Cellase 1000) concentration was 400 ppm. based on the HEC, the large amount of enzyme making them accelerated tests. Degradation was at 25° C. for 4 hours in closed containers. The following Table VI gives a comparison of properties.

TABLE VI

	Example 12 This Invention HEC	Example 13 Prior Art HEC
M.S.	2.9	2.9
Brookfield Viscosity, cps, on 1% aqueous solutions at 25°C.	800	790
% anhydroglucose units unsubstituted	5.1	8.5
Viscosity after 4 hours	120	10
% viscosity retained after accelerated enzymatic degradation	15	1.2

Generally, a water-based latex paint comprises finely divided pigment material and a finely divided film former, both of which are dispersed in a liquid vehicle consisting essentially of water. Dissolved in the liquid vehicle is a suspending agent.

The finely divided pigment material consists essentially of at least one pigment. It can include a mixture of pigments and extenders, examples of which are titanium dioxide, calcium carbonate and china clay.

The finely divided film former or binder consists essentially of at least one film forming organic substance. Generally, it is supplied dispersed in a liquid medium, usually comprising water, and the dispersion frequently is referred to as an emulsion or latex. When the liquid medium is substantially removed, for example by evaporation as when the dispersion is applied as a coating to a surface, the film former coalesces to form a resinous or polymeric film.

The suspending agent increases the consistency and/or the viscosity of the liquid vehicle and thereby minimizes settlement of the particles dispersed or suspended in the liquid vehicle and makes it easier to apply.

In addition to the foregoing components, these latex paints also usually comprise surfactant material having a dispersant function and a wetting agent function. A primary purpose of the dispersant function is to minimize flocculation or coagulation of dispersed particles prior to application to a surface to be painted, while a primary purpose of the wetting agent function is to facilitate adherence of the paint to oily surfaces. Usually, but not necessarily, the surfactant material comprises two or more substances, at least one of which acts primarily as a dispersant and at least another of which acts primarily as a wetting agent. Part or all of the surfactant material can be present in the dispersion

of film former as supplied to the paint formulators.

In summary, this invention provides a protective coating composition comprising (1) a film former dispersed in (2) a liquid vehicle consisting essentially of water and (3) dissolved in said liquid vehicle a suspending agent consisting essentially of hydroxyethyl cellulose having certain improved and very desirable properties for use in said composition. These three components are the essential components of the basic composition of this invention. In other words, no other components need be present. However, a preferred general embodiment of this basic composition comprises (4) pigment material dispersed in the liquid vehicle. In addition, preferred specific embodiments comprise (5) surfactant material having at least a dispersant function and preferably a wetting agent function. Additives, for example, a preservative or a foam depressant can also be present.

The film former, as previously defined herein, is at least one film-forming organic substance. Examples of a film-forming organic substance include polymer substances, particularly rubberlike or elastomeric materials, obtainable in stable aqueous latex form and capable of coalescing into a film, preferably a pigmented film, when brushed, sprayed, rolled or otherwise deposited on a surface at normal room conditions.

Particularly applicable are natural rubber latex, polymeric materials made by emulsion polymerization, and polymers dispersed in water as by emulsification of a solvent solution of a polymer followed by partial or complete removal of the solvent by evaporation. Included e.g. are: vinyl polymers, especially the homopolymers and copolymers of vinyl acetate, vinyl chloride, vinylidene chloride and copolymers with other unsaturated monomers e.g. ethylene, propylene, maleate and fumarate

esters and acrylic esters; homopolymers and copolymers of olefin hydrocarbons, e.g. ethylene, propylene, 1-butene, styrene, butadiene and isoprene, examples of such polymers including polyethylene, polypropylene, polystyrene, polybutadiene, polyisoprene, butadiene-styrene copolymer, butadiene-vinyl toluene copolymer, isoprene-styrene copolymer, as well as oxidized and halogenated derivatives of these homopolymers and copolymers for instance oxidized polyethylene and chlorinated polyisoprene; acrylic homopolymers and copolymers, containing recurring units of an acrylic acid ester, methacrylic acid ester, acrylonitrile and the like units; alkyd resins; and nitrocellulose. Preferred film formers include e.g. vinyl acetate homopolymer, vinyl acetate copolymers with dibutyl and dioctyl maleate and fumarate, vinyl acetate-ethylene copolymer vinyl acetate-acrylic and methacrylic ester copolymers, homopolymers and copolymers of methyl, ethyl and butyl acrylates and methacrylates, and butadiene-styrene copolymers.

The amounts of HEC, film former and water (by weight of the total protective coating composition) which may be used vary widely. Generally amounts of HEC of 0.03%—3.0%,

preferably 0.2—0.7%, are suitable. Generally amounts of film former of 10%—35%, preferably 15%—25%, are suitable. Generally amounts of water 30%—65%, preferably 35%—50%, are suitable.

As the artisan will readily appreciate all he needs to know to realize the full benefits of the present invention is to substitute the HEC hereof for prior art HEC in protective coating compositions, the prior art has extensively practiced and published the preparation and use of protective coating compositions for many years using prior art HEC. Thus nothing needs to be taught regarding ingredients, amounts, protective coating composition, preparation and use, and so forth.

WHAT WE CLAIM IS:—

1. A protective coating composition comprising a film former dispersed in water and a suspending agent consisting of a hydroxyethyl cellulose which has an M.S. (as hereinbefore defined) in the range of 1.5 to 10 and a maximum percentage unsubstituted anhydroglucose unit content as defined by the following tabulation in which each M.S. range includes the first value but excludes the last value:

	M.S. Range	Maximum % Anhydroglucose Units Unsubstituted
	1.5 and all values between 1.5 and 2.0	11
60	2.0 and all values between 2.0 and 2.5	9
	2.5 and all values between 2.5 and 3.0	7
	3.0 and all values between 3 and 3.5	5.5
	3.5 and all values between 3.5 and 4.0	4
	4.0 and all values between 4.0 and 5.0	2
65	5.0 and all values between 5.0 and 10	1

2. An improved protective coating according to claim 1, in which said protective coating composition contains hydroxy-ethyl cellulose, film former and water, respectively, in the amount of 0.03%—3.0%, 10%—35%, and 30%—65% by weight of the total protective coating composition.

3. An improved protective coating according to either of claims 1 and 2, in which the hydroxyethyl cellulose component of the composition is prepared by carrying out the hydroxylation in two stages, the first stage being carried out at an alkali/cellulose ratio of at least 0.2/1, and in the second stage the ratio not being in excess of 0.1/1.

4. An improved protective coating according to any one of the preceding claims, in

which the hydroxyethyl cellulose has an M.S. of between 2.5 and 3.0 and the maximum percentage unsubstituted anhydroglucose unit content is 7.

5. A method of increasing the biostability of a water-based protective coating composition, said composition comprising a film former dispersed in water and a suspending agent consisting of a hydroxyethyl cellulose, comprising using as the suspending agent a hydroxyethyl cellulose having an M.S. (as hereinbefore defined) in the range of 1.5 to 10 and a maximum percentage unsubstituted anhydroglucose unit content as defined by the following tabulation in which each M.S. range includes the first value but excludes the last value:

	<i>M.S. Range</i>	<i>Maximum % Anhydroglucose Units Unsubstituted</i>
	1.5 and all values between 1.5 and 2.0	11
5	2.0 and all values between 2.0 and 2.5	9
	2.5 and all values between 2.5 and 3.0	7
	3.0 and all values between 3 and 3.5	5.5
	3.5 and all values between 3.5 and 4.0	4
	4.0 and all values between 4.0 and 5.0	2
10	5.0 and all values between 5.0 and 10	1

6. A method according to claim 5, in which the hydroxyethyl cellulose has an M.S. of between 2.5 and 3.0 and the maximum percentage unsubstituted anhydroglucose unit content is 7.
7. A method according to claim 5 or 6 in which the hydroxyethyl cellulose component of the composition is prepared by carrying out the hydroxylation in two stages, the first stage being carried out at an alkali/cellulose ratio of at least 0.2/1, and in the second stage the ratio not being in excess of 0.1/1.
8. Protective coating compositions substantially as hereinbefore described with reference to any one of Examples 1, 3, 5, and 12.
9. Protective coating compositions according to any one of claims 1 to 4, substantially as hereinbefore described.
10. A method of increasing the biostability of a water-based protective coating composition, substantially as hereinbefore described in any one of the foregoing Examples 1, 3, 5 and 12.
11. A water-based protective coating composition the biostability of which has been increased by the method of any one of claims 5 to 7 and 10.

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